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Effect of composition on the structure and piezoelectricity of $Na_{0.5}Bi_{4.5}Ti_4O_{15}$-based flexoelectric-type polar ceramics

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ABSTRACT

Flexoelectric-type polar ceramics might specify a class of heterogeneous ceramics that possess permanent, macroscopic, flexoelectric-type polarization and thus can exhibit both direct and converse piezoelectric effects without undergoing an electrical poling process. Here we show, by studying series of $Na_{0.5}Bi_{4.5}Ti_4O_{15}$-based nominal compositions, that flexoelectric-type polar ceramics can be synthesized by adding an appropriate amount of excess Bi_2O_3 to $Na_{0.5}Bi_{4.5}Ti_4O_{15}$, whereas the addition of only excess Na_2CO_3 or excess TiO_2 to $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ does not have this effect. The obtained $Na_{0.5}Bi_{4.5}Ti_4O_{15} + xBi_2O_3$ flexoelectric-type polar ceramics all contain $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ and $Bi_{12}TiO_{20}$ phases, and their macroscopic polarization might originate from the partial alignment of distorted TiO_6 octahedra and BiO_5 polyhedra that are located within the grain boundary amorphous phases. Because the sodium-modified $Na_{0.5}Bi_{4.5}Ti_4O_{15} + 2.25Bi_2O_3$ flexoelectric-type polar ceramics were found to have a piezoelectric coefficient, d_{33}, larger than 8 pC/N and a depoling temperature higher than 700 °C, they are thought to have potential piezoelectric applications in the high-temperature region.

1. Introduction

Traditional piezoelectric ceramics belong to the class of ferroelectric polycrystalline materials. They all undergo an electrical poling process and thus can exhibit piezoelectricity due to the orientation of the ferroelectric spontaneous polarization [1]. In fact, non-ferroelectric polycrystalline materials also have the potential to be piezoelectrics due to the presence of flexoelectricity [2–6] (coupling between the electric polarization and strain gradient). In principle, the flexoelectric effect exists in all dielectrics; however, this effect is generally ignored because its influence on the electric polarization is very small for homogeneous, bulk, three-dimensional solids [7]. In recent years, the flexoelectric effect has attracted much attention due to the successful development of large flexoelectric polarization in low-dimensional or inhomogeneous materials, in which a large strain gradient can be easily generated and even sustained. These materials include thin films [8,9], superlattices [10], nanocomposites [3,5,6] and other nanostructures [11–13], and their excellent ferroelectric or piezoelectric properties indicate the potential utilization of flexoelectricity in the design of new, artificial polar materials.

Recently, we have found that some sintered, bulk composite ceramics that contain a perovskite phase (such as ferroelectric $Na_{0.5}Bi_{0.5}TiO_3$, non-ferroelectric $SrTiO_3$ and their solid solutions) and a sillenite $Bi_{12}TiO_{20}$ phase can exhibit both direct and converse piezoelectric effects without undergoing an electrical poling process [14–16]. These special, polar, heterogeneous ceramics should possess a permanent macroscopic electric polarization that is most likely induced by a strain gradient; thus, we have tentatively called them flexoelectric-type polar ceramics. Although we have proposed a possible poling mechanism for this new type of polar ceramic [16], the roles played by different phases in these heterogeneous materials remain unclear. In the present work, we investigate a new system of flexoelectric-type polar ceramics, using the following nominal composition formulas: $Na_{0.5}Bi_{4.5}Ti_4O_{15} + xNa_2CO_3$ (NBT–*x*Na), $Na_{0.5}Bi_{4.5}Ti_4O_{15} + xBi_2O_3$ (NBT–*x*Bi), $Na_{0.5}Bi_{4.5}Ti_4O_{15} + xTiO_2$ (NBT–*x*Ti), $Na_{0.5}Bi_{4.5}Ti_4O_{15} + 2.25Bi_2O_3 + xNa_2CO_3$ (NBT–Bi–*x*Na), and $Na_{0.5}Bi_{4.5}Ti_4O_{15} + 2.25Bi_2O_3 + xTiO_2$ (NBT–Bi–*x*Ti). In particular, we focus on the effect of composition on the structure and piezoelectricity of these composite ceramics.

2. Experimental procedures

The NBT–*x*Na (x = 0.2, 0.25, 0.33, 0.5), NBT–*x*Bi (x = 0.5, 1, 2, 2.25, 2.5, 3, 4, 5, 6), NBT–*x*Ti (x = 1, 4, 10, 20), NBT–Bi–*x*Na (x = 0, 0.15, 0.25, 0.35, 0.5), and NBT–Bi–*x*Ti (x = 0.5, 1, 2, 3) ceramics were fabricated by the conventional sintering technique. Corresponding amounts of Bi_2O_3 (99.8%), TiO_2 (99.8%) and Na_2CO_3 (99.8%) were weighed and ball-milled in alcohol for 12 h. The dried powders with different compositions were pressed into blocks and then calcined at suitable temperatures (750–800 °C) for 4 h. After calcination, the blocks were ground, wet-milled, dried and pressed into 15-mm-diameter disks. These disks with different compositions were sintered at optimized temperatures (800–940 °C) and then naturally cooled to room temperature. The piezoelectric coefficient d_{33} was measured using a

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YE2730A d_{33} meter along the thickness direction of these ceramic disks. The piezoelectric resonance signals were recorded using an Agilent 4294A impedance analyzer. The constituent crystalline phases and the microstructures of the ceramics were studied with an X-ray diffractometer (XRD) (Bruker AXS D8 Advance) and a high-resolution scanning electron microscope (SEM) (Hitachi S-4800). The local structures and chemical-bonding environments were analyzed using Raman spectroscopy (Horiba Jobin–Yvon, LabRAM HR-800).

3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns of the NBT–0.2Na, NBT–3Bi and NBT–1Ti ceramics, and more information about the constituent crystalline phases and piezoelectric activity of these sintered ceramics is summarized in Table 1. Among the NBT–xNa, NBT–xBi and NBT–xTi ceramics, only the NBT–xBi ceramics were found to have piezoelectricity without undergoing an electrical poling process. This result indicates that adding an appropriate amount of excess Bi_2O_3 to $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ can yield flexoelectric-type polar ceramics that most likely possess a permanent macroscopic polarization, whereas only adding excess Na_2CO_3 or excess TiO_2 in $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ does not have this effect. Notably, the appearance of macroscopic polarization may be closely related to the coexistence of the $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ and $Bi_{12}TiO_{20}$ crystalline phases that appear in the NBT–xBi ceramics. For the NBT–xNa system, a small amount of excess sodium ions may be prone to forming sodium-related amorphous phases. Thus, for the $x \leqslant 0.25$ samples, we did not detect any other sodium-related crystalline phases, except for $Na_{0.5}Bi_{4.5}Ti_4O_{15}$. Upon further increase of the sodium content ($x \geqslant 0.33$), $Na_{0.5}Bi_{0.5}TiO_3$ and Bi_2O_3 phases appeared, and their contents gradually increased along with the decrease of the $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ phase. For the NBT–xTi system, the $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ phase gradually disappeared with increasing titanium content, but $Bi_2Ti_2O_7$ and TiO_2 appeared. In the NBT–4Ti, NBT–10Ti and NBT–20Ti ceramics, sodium could not be detected in any crystalline phases, which may also have been due to the formation of sodium-related amorphous phases. Because the $Bi_{12}TiO_{20}$ crystalline phase was not found in the NBT–xNa and NBT–xTi ceramics, we propose that excess Bi_2O_3, which is prone to self-synthesizing $Bi_{12}TiO_{20}$ [17] in the NBT–xBi ceramics, may help to form the permanent macroscopic polarization.

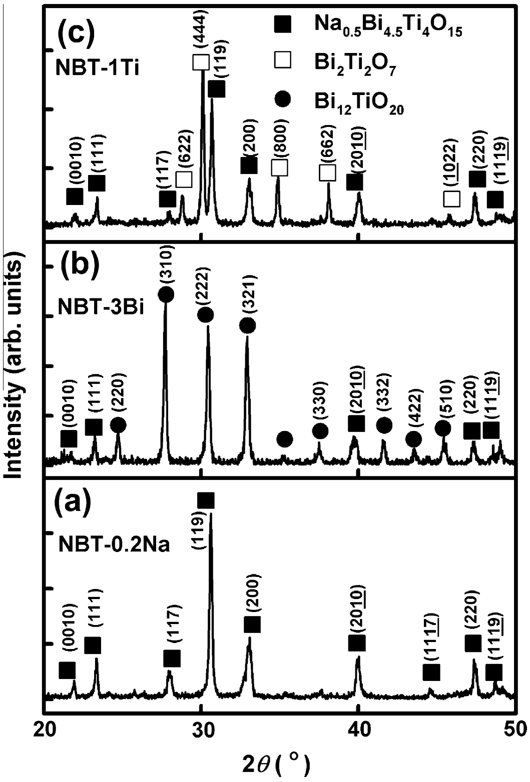

Fig. 1. The XRD patterns of the (a) NBT–0.2Na, (b) NBT–3Bi, and (c) NBT–1Ti ceramics.

For the NBT–xBi ($x \leqslant 4$) system, because most of the excess Bi_2O_3 could self-synthesize $Bi_{12}TiO_{20}$, and only $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ and $Bi_{12}TiO_{20}$ crystalline phases were detected, the larger x value generally means a higher $Bi_{12}TiO_{20}$ content in the sintered ceramics. It was found that, in the NBT–xBi system, the composite ceramics that contained a moderate amount of $Bi_{12}TiO_{20}$ ($2.25 \leqslant x \leqslant 2.5$) and had a relatively high density ($\rho \geqslant 7.2$ g/cm^3) could exhibit a maximum d_{33} value of approximately 4 pC/N. Too much $Bi_{12}TiO_{20}$ inclusion could result in a sharp decrease in density ($\rho \leqslant 6.6$ g/cm^3) of the NBT–xBi ($x \geqslant 3$) ceramics due to severe melting, which may explain the decrease in piezoelectric activity for these particular polar materials.

Fig. 2a and b shows the x dependence of the d_{33} values in the NBT–Bi–xNa and the NBT–Bi–xTi ceramics, respectively. The d_{33} value increases from 4.3 to 8.2 pC/N with increasing sodium content in the NBT–Bi–xNa system, whereas it decreases from 4.3 pC/N to zero with increasing titanium content in the NBT–Bi–xTi system. The typical XRD patterns of the NBT–Bi–xNa ceramics ($x = 0$ and $x = 0.5$) are shown in Fig. 3a and b, respectively. Additional information about the crystalline phases of the NBT–Bi–xNa and NBT–Bi–xTi ceramics is summarized in Table 2. In the NBT–Bi–xTi system, the $Bi_{12}TiO_{20}$ content decreased with increasing titanium content. The disappearance of $Bi_{12}TiO_{20}$ accompanied the disappearance of piezoelectricity, which further confirms the crucial role of $Bi_{12}TiO_{20}$ in these flexoelectric-type polar ceramics. In the NBT–Bi–xNa system, when $x \geqslant 0.35$, the third crystalline phase, $Na_{0.5}Bi_{0.5}TiO_3$, was observed, as shown in the inset of Fig. 3b. The phase transformation from $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ to $Na_{0.5}Bi_{0.5}TiO_3$ can be described as follows:

$$4Na_{0.5}Bi_{4.5}Ti_4O_{15} + 3Na_2CO_3 \rightarrow 16Na_{0.5}Bi_{0.5}TiO_3 + 5Bi_2O_3 + 3CO_2$$

Because self-synthesizing $Na_{0.5}Bi_{0.5}TiO_3$ can consume less bismuth than self-synthesizing $Na_{0.5}Bi_{4.5}Ti_4O_{15}$, the content of self-synthesized $Bi_{12}TiO_{20}$ may increase with the increasing x value in the NBT–Bi–xNa system. Thus, the higher content of $Bi_{12}TiO_{20}$ and the relatively high density ($\rho \geqslant 6.9$ g/cm^3) may partially explain the higher d_{33} value in this system.

Fig. 4 shows the Raman spectra of the NBT–Bi–0.5Na, NBT–Bi–0.5Ti, $Bi_{12}TiO_{20}$ and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ ceramics. The $Bi_{12}TiO_{20}$ and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ ceramics were reference samples that were also fabricated by the conventional sintering technique and confirmed by XRD. The Raman peaks of these $Na_{0.5}Bi_{4.5}Ti_4O_{15}$-based flexoelectric-type polar ceramics can be divided into two groups: the $Bi_{12}TiO_{20}$-related peaks labeled P1–P15 and the $Na_{0.5}Bi_{4.5}Ti_4O_{15}$-related peaks labeled P16 and P17. Some Raman peaks of $Bi_{12}TiO_{20}$ are very strong, and thus they overlap with $Na_{0.5}Bi_{0.5}TiO_3$-related peaks in the Raman spectrum of the NBT–Bi–0.5Na ceramic [18–20]. As is well known [21,22], the framework of the $Bi_{12}TiO_{20}$ structure is formed by sharing-edges distorted BiO_5 polyhedra forming dimers. The coordination sphere of Bi atoms consists of five different oxygen atoms – O(1a), O(1b), O(2), O(1c), and O(3). The Ti atoms located at the vertices and in the center of the cubic lattice are coordinated with O(3) atoms and form regular TiO_4 tetrahedral. Because $Bi_{12}TiO_{20}$ has very complicated structure, there is still no unified explanation for all its Raman modes. However, we can confirm that the P1–P12 and P13–P15 peaks are related to BiO_5 and TiO_4, respectively. One detailed explanation for the Raman spectrum of $Bi_{12}TiO_{20}$ can be found in Ref. [21]. Compared with those of the $Bi_{12}TiO_{20}$ ceramic, the P1, P3, P4 and P12 peaks of the